HIGH TEMPERATURE SKARNS IN THE MARONIA AREA (NE GREECE)

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ABSTRACT

High temperature skarns are formed at the western contact zone of the Maronia mon-zogabbro with the calcarous phyllites and the marbles.They are Ca- and Al-rich and poor in Fe. Melilite skarns are formed at the innermost contact zone by the reaction of the marble with the melt at temperatures higher than 900°C. They consist predominantly of melilite (gehlenite 40-70%, aker-manite 30-55%, Na-melilite 0-10%). Wollastonite, larnite , calcite and grossular-andradite garnet occur in subordinate amounts. During cooling, melilite decomposes into gehlenite + monticellite + grossular at temperatures lower than 850°C and at still lower tempera-tures (between 575-625°C) it is replaced by vesuvianite + corundophyllite.

Diopside-wollastonite-vesuvianite-grossular skarns are formed from calcareous phyllites, possible at temperatures between 700-775°C. Melilite(?) and akermanite(?) are formed within the stability field of grossular + calcite. In a retrograde stage akermanite breaks down to diopside + calcite and melilite is replaced by vesuvianite.

In augite-grossular skarns, augite is exceptionally rich in Al_2O_3, with a Ca-Tschermak's component ranging from 3.7 to 21%.

ΠΕΡΙΛΗΨΗ

Στην περιοχή της Μαρώνειας σχηματίστηκαν skarns υψηλών θερμοκρασιών στην δυτική επαφή του μονζογάββρου με τους ασβεστιτικούς φυλλίτες και τα μάρμαρα. Τα skarns είναι πλούσια σε Ca και Al και φτωχά σε Fe.

Τα μελιλιθικά skarns σχηματίστηκαν στην εσωτερική ζώνη επαφής, σε θερμοκρασίες υψηλότερες των 900°C, από την αντίδραση των μαρμάρων με το τήγμα. Αποτελούνται κατεξοχή από μελίλιθο (γκελενίτης 40-70%, ακερμανίτης 30-55%, Na-μελίλιθος 0-10%). Βολλαστονίτης , λαρνίτης, ασβεστίτης και γρανάτης (σύστασης γροσσουλάριου-ανδραδίτη) συμμετέχουν σε πολύ μικρό ποσοστό. Κατά την ψύξη, σε θερμοκρασίες κάτω των 850°C, ο μελίλιθος διασπάστηκε σε γκελενίτη + μοντισελλίτη + γροσσουλάριο και σε ακόμα χαμηλότερες (μεταξύ 575-625°C) αντικαταστάθηκε από βεζουβιανίτη και κορουνδοφυλλίτη.

Τα skarns διοψιδίου - βολλαστονίτη - βεζουβιανίτη - γροσσουλάριου σχηματίστηκαν από ασβεστιτικούς φυλλίτες σε θερμοκρασία μεταξύ 700-775°C. Ο μελίλιθος (;) και ο ακερμανίτης (;) σχηματίστηκαν στο πεδίο σταθερότητας του γροσσουλάριου + ασβεστίτη. Κατά την ψύξη ο ακερμανίτης αντικαταστάθηκε από διοψίδιο + ασβεστίτη και ο μελίλιθος από βεζουβιανίτη.

Στα skarns αυγίτη-γροσσουλάριου, ο αυγίτης είναι ιδιαίτερα πλούσιος σε Al_2O_3. Το ποσοστό συμμετοχής του Ca-τσερμακιτικού μορίου κυμαίνεται μεταξύ 3,7-21%.

INTRODUCTION

The term skarn includes a large variety of calc-silicate rocks rich in calcium, iron, or mag-nesium formed by replacement of initially calcium-rich rocks (Einaudi et.al.,1982).

High temperature skarns are relatively uncommon and have been reported at 25 locations in the world. They are formed at the contact zones of shallow basic intrusions with carbonate bearing rocks ; i.e. in Inverness-shire , Great Britain between olivine gabbro and limestones leading to the -

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formation of a monticellite+merwinite+gehlenite+calcite paragenesis (Tilley, 1947), or at the Anakit district in Russia between a shallow dolerite intrusion and carbonate bearing rocks leading to the mineral associations: wollastonite-rankinite, rankinite-spurrite-melilite,spurrite-melilite merwinite-calcite, merwinite-monticellite-melilite-calcite (Reverdatto et al.,1979).

The present work deals with a new occurence of high temperature skarns in the area of Maronia (NE Greece) formed at the western contact zone of the Maronia monzogabbro (Doryphoros, 1990) and the surrounding marbles and calcareous phyllites.

GEOLOGICAL SETTING

The Maronia area belongs to the Circum Rhodope Belt and was mapped by Papadopoulos (1982). In this area the Circum Rhodope Belt comprises the Makri Series consisting of marbles, calcareous schists, gneisses, quartzites, muscovite schists, chlorite-epidote schists and greenschists, which have undergone a lower-greenschist facies regional metamorphism. The Tertiary magmatic activity in the area is evidenced by acidic vulcanity and the intrusion of the Maronia monzogabbro dated by Kyriakopoulos (1987) by Rb-Sr method at 28.9±0.1 my.
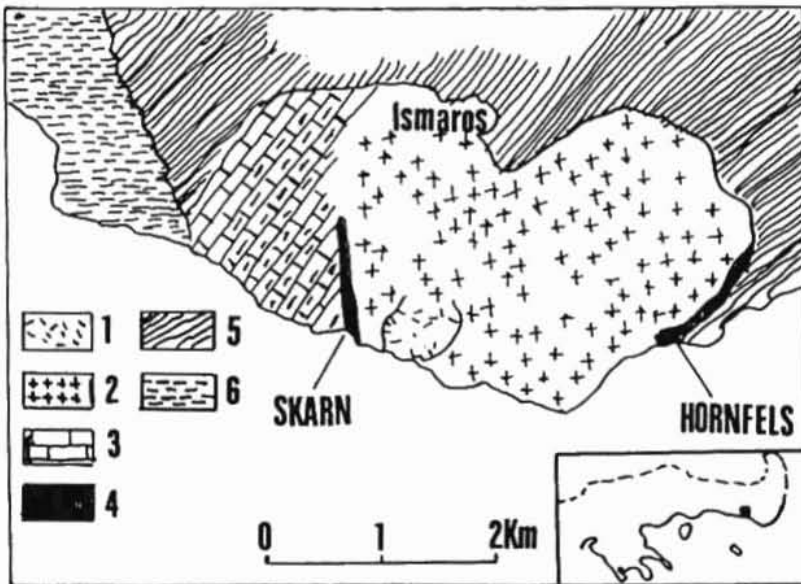

Fig.1: Simplified geological map of the area of the Maronia plutonite compiled with data of Sideris (1975) and Andronopoulos (1966). 1: rhyolite, 2: monzogabbro, 3:marbles, 4: contact zone with hornfelses and skarns, 5: Makri series (undifferentiated), 6: Tertiary sediments.

THE MARONIA MONZOGABBRO

The monzogabbro of the Maronia area forms part of the Ismaros mountain . It is medium-grained, and consists of plagioclase, orthoclase, augite, biotite and small amounts of quartz.In some samples hornblende and orthopyroxene were identified. Apatite, sphene, magnetite and pyrite are present as accessory minerals.

Plagioclase forms euhedral tabular crystals showing normal compositional zoning with

An-contents ranging from 70% in the core to 45% in the rim. This type of zoning indicates a shallow intrusion. Plagioclase commonly encloses biotite, pyroxene, small grains of plagioclase and apatite, and in turn formes inclusions in pyroxene, biotite and usually in orthoclase.

Augite occurs as euhedral crystals containing plagioclase, biotite and magnetite inlusions. It is replaced by magnesio-hornblende and in a subsequent stage, by actinolitic hornblende and chlorite. The wollastonite component in augite ranges from 33.4-43.8 mol%, the enstatite component from 36.4-41.7 mol% and the ferrosilite component from 7.5-11.5 mol %.It is relatively poor in TiO_2 ranging between 0.27-0.70%. Al_2O_3 ranges between 0.78-1.84%.

Biotite forms euhedral reddish-brown crystals, commonly containing plagioclase, augite, magnetite , and apatite inclusions. It is rich in titanium ranging from 0.47 to 0.59 atoms p.f.u. (per formula unit), calculated on the basis of 22 oxygen atoms. Part of the iron is in its trivalent state occupying tetrahedral sites (0.05-0.16 atoms p.f.u.; Doryphoros, 1990).

Orthoclase is poikilitic with plagioclase , augite, biotite, apatite, sphene and magnetite inclusions. It occupies the interstitial space between the main mineral phases. The albite component in orthoclase ranges between 11.0-24.8 mol % and the anorthite component between 1.6-3.5 mol %.

THE SKARNS

The Maronia plutonic intrusion caused thermal metamorphic phenomena on its eastern contact zone and, in addition, contact metasomatic phenomena on its western contact zone. Among the rock types that were affected, the metamorphic and metasomatic phenomena are most intense in the marbles and in the calcareous phyllites. At the eastern contact zone the calcareous phyllites formed calc-silicate hornfesles with characteristic parageneses : diopside+basic plagioclase and diopside+biotite+basic plagioclase+brown hornblende. In addition, at the western contact zone, the marbles and the calcareous phyllites formed high temperature skarns.

The Maronia skarns form a narrow zone delineating the Maronia pluton border having a thickness of 3-5m. The absense of ferrous minerals in the skarn zone is responsible for its light colouration.

Depending on the bulk rock chemistry the distance from the plutonic body and the degree of metasomatism the folowing main rock types are distinguished.

1. Diopside-plagioclase-orthoclase hornfels.

It presents the following mineral assemblage:

diopside-plagioclase-orthoclase-biotite-magnetite ± clinoziosite.

This rock type exhibits a weak layering with alternating anorthite rich and diopside rich layers. The presence of orthoclase instead of muscovite suggests that the metamorphic conditions exceeded those indicated by the reaction:

muscovite + calcite + quartz = K-feldspar + anorthite + CO_2 + H_2O

According to Hewitt (1973) the above reaction takes place at temperatures higher than 400°C for a pressure of 1Kbar assuming $X_{CO2}=0.5$.

2. Clinopyroxene-wollastonite-grossular skarn.

This skarn type is represented by the following mineral assemblage:

grossular-wollastonite-diopside-augite-calcite ± orthoclase

A layering like that observed in the diopside-anorthite-orthoclase hornfels is also present in this rock type, with grossular rich layers alternating with diopside+wollastonite rich ones.

Wollastonite occurs in large prismatic crystals often in association with grossular+calcite. Wollastonite and calcite inclusions in grossular are also common. These textural relations suggest that the mineral association grossular+calcite+wollastonite is a stable one, indicating that

the metamorphic conditions exceed those characterized by the reaction:

anorthite + wollastonite + calcite = grossular + CO_2

The absence of anorthite indicates the complete consumption of this phase during the progress of the above reaction.

3. Diopside-wollastonite-vesuvianite-grossular skarn.

In this rock type wollastonite is a main phase forming large prismatic crystals. It shows often resorbed edges and is replaced by grossular. Diopside occurs in association with calcite in the form of unoriented thin prismatic aggregates replacing pseudomorphically an unknown phase (possibly akermanite).

Two kinds of garnets are identified. (a) Medium grained idiomorphic grossular crystals commonly in association with calcite. They contain inclusions of wollastonite and calcite. (b) Small vermicular garnets filling the interstitial space between vesuvianite crystals.
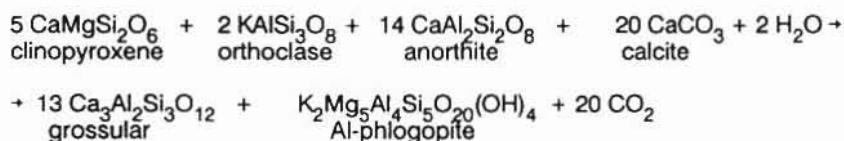
Vesuvianite is concentrated in some layers in which it forms a main mineral phase. It often contains inclusions of wollastonite, calcite and idiomorphic grossular garnets. The presence of vermicular garnet in the interstitial space of vesuvianite crystals, known from bodies of melilite skarn (see below), and the fact that it includes all the other phases suggest that vesuvianite is formed in a late stage possibly by hydration of previous melilite.

The textural relations described above indicate that the minerals in this rock type are formed with the following succession: wollastonite + calcite + (diopside + anorthite) - garnet- (melilite) - (akermanite) - diopside (aggregates) + calcite - vesuvianite.

4. Al-phlogopite-grossular skarn.

This skarn type is formed by interaction between the monzogabbro and the marble with influx of water. It consists predominantly of grossular and Al-phlogopite (see mineral chemistry). Calcite and chlorite occur in small amounts.

In this skarn type grossular + phlogopite may have formed according to the following reaction :

$$5\ CaMgSi_2O_6\ +\ 2\ KAlSi_3O_8\ +\ 14\ CaAl_2Si_2O_8\ +\ 20\ CaCO_3\ +\ 2\ H_2O \rightarrow$$
clinopyroxene   orthoclase   anorthite   calcite

$$\rightarrow\ 13\ Ca_3Al_2Si_3O_{12}\ +\ K_2Mg_5Al_4Si_5O_{20}(OH)_4\ +\ 20\ CO_2$$
grossular   Al-phlogopite

5. Augite-grossular skarn.

The main mineral phases in this skarn type are grossular, augite and calcite. Augite occurs in idiomorphic prismatic crystals often with a compositional zoning. It is exceptionally rich in Al_2O_3 (up to 10.9%) and often rich in TiO_2 (up to 2.7%) (see mineral chemistry).

In this rock type, relics of magmatic augite containing biotite and apatite inclusions and sagenite exsolutions are preserved. Augite shows zoning with a pale green-coloured core and a colourless rim. Aggregates of calcite and fine grained quartz replace plagioclase pseudomorphically. Dark-brown titaniferous grossular-andradite garnet with numerous apatite inclusions is formed at the expense of biotite.

6. Melilite skarn

The melilite skarn bodies in Maronia are exceptionally interesting. They occur in the innermost contact zone between marble and monzogabbro. The thickness of the melilite skarns ranges from a few cm up to 2 meters. In handspecimen they exhibit a uniform grey colour and conchoidal fracture. The rock is medium grained and consists of equigranular melilite crystals having a typical granoblastic texture.

Melilite contains small inclusions of wollastonite, larnite and calcite. Wollastonite inclusions occur as isolated grains, while larnite inclusions are often associated with calcite. In one case
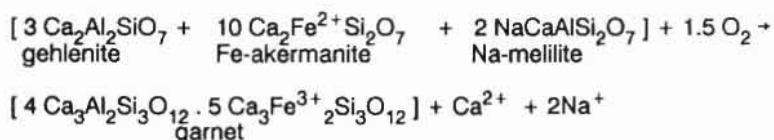
the three minerals are observed as inclusions in a melilite crystal . In this case, larnite occurs between calcite and wollastonite separating the other two phases. This textural relation verifies the larnite formation at the expence of wollastonite according to the reaction:

$$CaSiO_3 \quad + \quad CaCO_3 \rightarrow \quad Ca_2SiO_4 + CO_2$$
wollastonite $\qquad$ calcite $\qquad$ larnite

    Larnite is also observed in association with calcite in the interstitial space between melilite crystals.

    Textural or mineralogical relics of the parent rock are absent in melilite skarns. The rock is macroscopically and microscopically homogeneous. It seems to be formed by reaction of the melt with the marble. The presence of larnite as inclusions in melilite, which requires for its formation temperatures higher than $1000°C$, as will be discussed later , strenghens this view.

    In the interstitial space of the melilite crystals small vermicular garnet is formed. It is a grossular-andradite garnet with a composition $gross_{42-47}$: $andr_{51-56}$. It is possible formed by reaction of the melilite rim with an oxidizing fluid. The reaction could be expressed as follows:

$$[3\ Ca_2Al_2SiO_7 + \quad 10\ Ca_2Fe^{2+}Si_2O_7 \quad + \quad 2\ NaCaAlSi_2O_7] + 1.5\ O_2 \rightarrow$$
gehlenite $\qquad$ Fe-akermanite $\qquad$ Na-melilite

$$[4\ Ca_3Al_2Si_3O_{12} . 5\ Ca_3Fe^{3+}{}_2Si_3O_{12}] + Ca^{2+} + 2Na^+$$
$\qquad\qquad$ garnet

    The formation of the vermicular garnet by this reaction could explain the compositional zoning observed in some melilites , where an increase in Mg and a decrease in Al and Na from the core to the rim is observed (see mineral chemistry).

    In the outer part of the melilite skarn bodies and along fractures melilite decomposes into a fine grained aggregate consisting of gehlenite, monticellite and grossular. In an advanced stage of retrogression vesuvianite+corundophyllite replace the melilite, leading to the formation of vesuvianite skarns.

MINERAL CHEMISTRY

Garnet

    Two garnet types are distinguished: a grossular garnet formed in all garnetiferous rock types except for the melilite skarns and a grossular-andradite garnet identified mainly in the melilite skarns. Representative compositions of both garnet types are listed in Table 1.

    The composition of the grossular garnet is: $Gross_{77-91}$ And_{7-21} Pyr_{0-2} $Spess_{<0.15}$ $Alm_{<1.7}$. The composition of the grossular-andradite garnet is: $Gross_{42-47}$ And_{51-56} $Spess_{<1.4}$ $Alm_{<0.7}$.

    Figure 2 shows the compositional variation of the garnets in relation to almandine+spessartine: grossular: andradite components. It is evident that garnet in the melilitic bodies shows a higher content in andradite component than in the grossular vesuvianite skarn and in the other skarn types.

Clinopyroxene.

    In calc-silicate hornfelses clinopyroxene is almost pure diopside. In the clinopyroxene-wollastonite skarn and in the augite-grossular skarn Al-rich or Al- and Ti- rich augite is also formed. Representative compositions of clinopyroxenes are given in Table 1.

    In the clinopyroxene-wollastonite-grossular skarn the Al_2O_3 content in augite ranges from 2.2% to 6.2% indicating a Ca-Tschermak's component substitution from 4 to 12 mol % (figure 3).

    In the augite grossular skarn the Al_2O_3 content in augite is exceptionally high ranging from 3.1% to 10.7%. TiO_2 ranges from 0.4% to 2.7%. The Ca-Tschermak's and Ca-Ti-Tschermak's components range from 3.6 to 21 mol % and 1.6 to 7 mol % respectively.

TABLE 1. Representative compositions of garnet and clinopyroxene in the skarns of Maronia area.

| | Garnet | | | | | Clinopyroxene | | | | |
	1	2	3*	4*		1*	2*	3*	4	5
SiO_2	39.40	39.51	37.99	37.91		45.57	45.08	52.00	53.05	52.87
TiO_2	-	-	0.39	0.89		2.02	1.79	0.18	0.24	0.39
Al_2O_3	20.35	20.45	8.45	8.47		8.59	7.69	5.59	1.62	2.65
Fe_2O_3	3.36	3.01	17.69	17.29		4.42	4.66	-	1.66	-
FeO	0.05	0.22	0.55	0.29		0.5	3.14	0.65	0.04	1.56
MnO	0.06	0.07	0.61	0.01		-	-	-	-	-
MgO	0.56	-	0.12	0.12		12.68	11.11	15.47	16.32	16.00
CaO	35.90	36.64	34.36	35.36		25.95	25.53	26.59	26.34	26.00
Total	99.68	99.90	100.16	100.34		99.73	99.0	100.78	99.27	99.47

Cations/oxygen atoms		(12)						(6)		
Si	2.99	2.99	3.03	3.00		1.691	1.709	1.875	1.934	1.933
Al	1.82	1.82	0.87	0.80		0.376	0.344	0.237	0.070	0.114
Ti	-	-	0.02	0.05		0.057	0.051	0.005	0.007	0.011
Fe^{3+}	0.19	0.17	1.00	1.07		0.124	0.133	-	0.046	-
Fe^{2+}	-	0.02	0.03	0.03		0.016	0.099	0.019	0.001	0.048
Mn	-	-	0.01	0.04		-	-	-	-	-
Mg	0.06	-	0.08	0.01		0.701	0.628	0.831	0.909	0.872
Ca	2.92	2.97	2.92	2.96		1.032	1.037	1.027	1.028	1.018

Alm	0.12	0.48	1.25	1.22	Ca-Tsch	17.53	17.64	10.07	4.34	4.26
Gros	88.00	90.59	45.21	41.67	Ca-Ti-					
Pyr	2.12	-	2.81	0.50	Tsch	5.27	4.81	0.46	0.64	1.05
Spes	0.13	0.15	0.39	1.37	Wo	42.66	43.30	48.12	49.01	49.23
Andr	9.63	8.78	50.35	55.24	En	32.75	29.56	39.13	44.58	42.59
					Fs	0.74	4.69	0.92	0.06	2.33

*vermicular garnet in melilite skarn   *Al-rich augite

Melilite

Representative compositions of melilite are listed in Table 2. Melilite usually has a homogenous composition ; however some crystals show zoning with Mg increase and Al and Na decrease from the core to the rim.

Figure 4A shows the compositional variation of the Maronia melilite in relation to gehlenite[$Ca_2Al_2SiO_7$, (Gehl)]: akermanite[$Ca_2MgAl_2Si_2O_7$,(Ak)] : soda melilite [$CaNaAlSi_2O_7$,(Smel)] components. The analysed melilites plot on or near the gehlenite-akermanite join. The Na-melilite component ranges from 0-10 mol %, the akermanite component from 30 to 55 mol % and the gehlenite component from 40 to 70 mol %. According to El-Goresy and Yoder (1973) melilites with gehlenite-akermanite composition are typical of metamorphic origin. The low Na-content of the Maronia melilites strengthens this view. The analyses plotted near the (Gehl) corner represent gehlenites formed as decomposition products of melilite, as mentioned in the previous chapter "the skarns". In Figure 4B the relationship Al: Mg of the melilites is presented. Gehlenites (triangles) plot almost on the gehlenite-akermanite tie-line, showing an akermanite component subsitution ranging from 5-11%. Most of the melilites (full circles) plot below the gehlenite-akermanite join, due to the presense of the Na-melilite component.
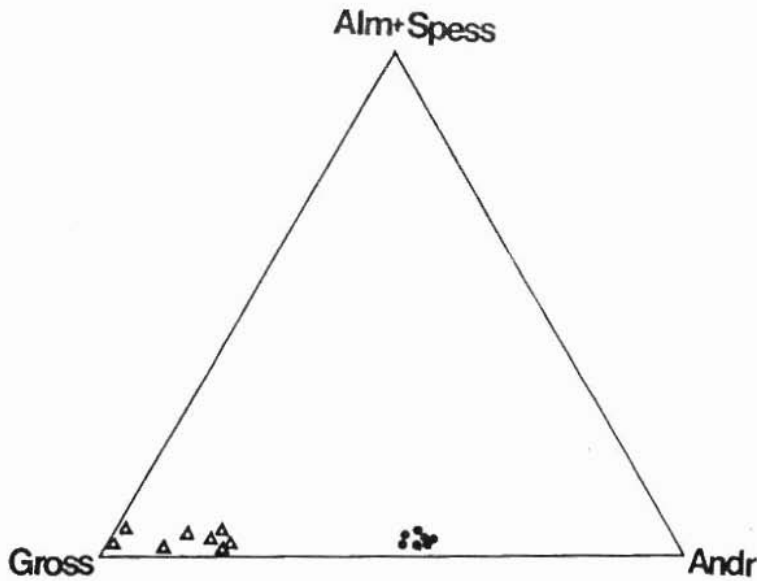
Fig.2: Chemical composition of garnets in relation to grossular (Gr): andradite (Ad): almandine+spessartine (Alm+Sp) components. ● garnet in melilite skarn, Δ = garnet in other skarn types.
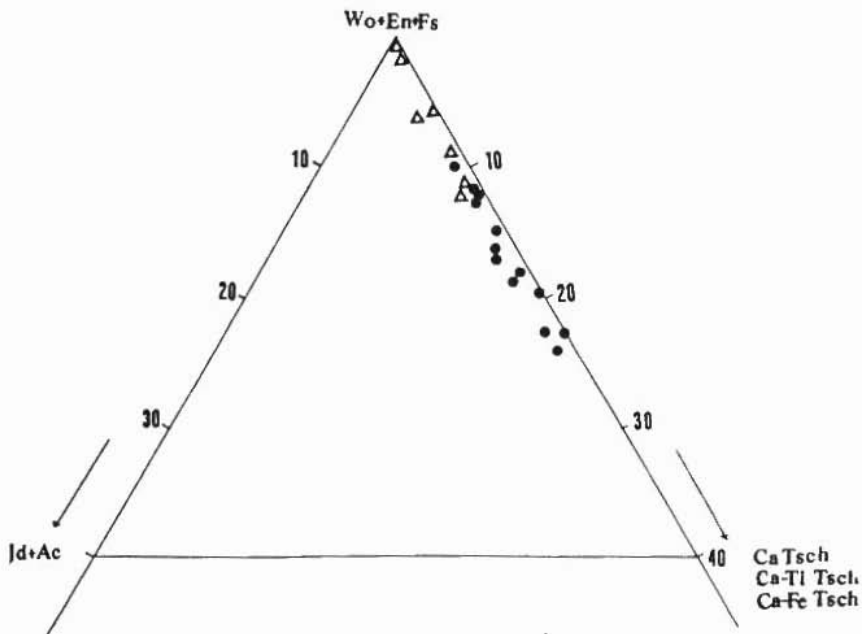

Fig.3: Chemical composition of clinopyroxenes in relation to Jadeite+acmite (Jd+Ac): wollastonite+enstatite+ferrosilite(Wo+En+Fs): Ca-Tschermak's+Ca-Ti-Tschermak's (Ca-Tsch+Ca-Ti-Tsch) components. Δ = in clinopyroxene-wollastonite-grossular skarn ● in augite-grossular skarn

Table 2. Representative compositions of melilite, vesuvianite, larnite, monticellite, chlorite and phlogopite in the skarns of Maronia area.

	Melilite				Gehle-nite	Larni-te	Montri-cellite		Vesuvi-anite		Chlo-rite	phlogo pite
	1(c)	2(r)	3(c)	4(r)	1	1	1	2	1	2	1	1
SiO_2	32.15	33.18	32.81	32.98	23.26	33.15	37.75	37.62	37.93	37.87	22.75	36.46
TiO_2	0.21	-	-	0.09	-	-	-	-	0.07	-	-	0.36
Al_2O_3	17.27	16.62	18.15	17.28	34.74	-	-	-	17.55	15.24	36.60	22.13
FeO^*	2.50	2.14	2.01	2.70	0.48	-	2.54	3.13	1.80	2.52	1.35	1.46
MnO	-	-	-	-	-	-	0.53	-	-	-	-	-
MgO	5.61	6.21	5.71	5.89	1.19	-	23.05	21.73	2.94	3.49	28.38	25.43
CaO	40.49	41.05	40.51	40.46	39.92	65.56	34.69	36.19	37.04	37.83	0.07	-
Na_2O	0.96	0.58	0.61	0.50	-	0.13	0.81	0.71	0.03	0.05	0.12	0.32
K_2O	0.09	0.17	-	0.10	0.42	-	0.63	0.64	-	-	-	10.72
Total	99.28	99.95	99.80	99.90	100.01	99.08	100.00	99.99	97.38	97.01	89.27	96.68
Cations/oxygen atoms	(7)						(4)		(72)		(28)	(22)
Si	1.50	1.53	1.50	1.52	1.06	1.00	1.00	1.00	17.89	18.10	4.14	5.05
Al	0.95	0.90	0.98	0.94	1.87	-	-	-	9.75	8.58	7.84	3.61
Ti	0.01	-	-	-	-	-	-	-	0.02	-	-	0.03
Fe^{2+}	0.08	0.08	0.07	0.10	0.02	-	0.05	0.06	0.71	1.01	0.20	0.16
Mn	-	-	-	-	-	-	0.01	-	-	-	-	-
Mg	0.32	0.42	0.40	0.40	0.08	-	0.91	0.86	2.06	2.48	7.69	5.21
Ca	2.02	2.03	1.99	2.00	1.95	2.04	0.98	1.03	18.72	19.38	0.01	-
Na	0.08	0.05	0.05	0.04	-	-	0.04	0.03	0.02	0.03	0.04	0.08
K	-	0.01	-	0.01	0.02	-	0.02	0.02	-	-	-	1.89

* Total iron as FeO

Larnite

According to representative microprobe analysis given in Table 2, its composition corresponds to almost pure larnite.

Al-Phlogopite

Phlogopite is associated parapenetically with grossular garnet, calcite, and seldom potassium feldspar. Representative analysis is given in Table 2. It is rich in Al , and poor in Ti, having a structural formula approaching that of the Al-phlogopite (Guidotti, 1984).

Monticellite

Monticellite is a decomposition product of melilite. Representative analyses are shown in Table 2. Fe^{2+} ranges between 0.05-0.06 atoms p.f.u. (calculated for 4 oxygen atoms), substituting for Mg.
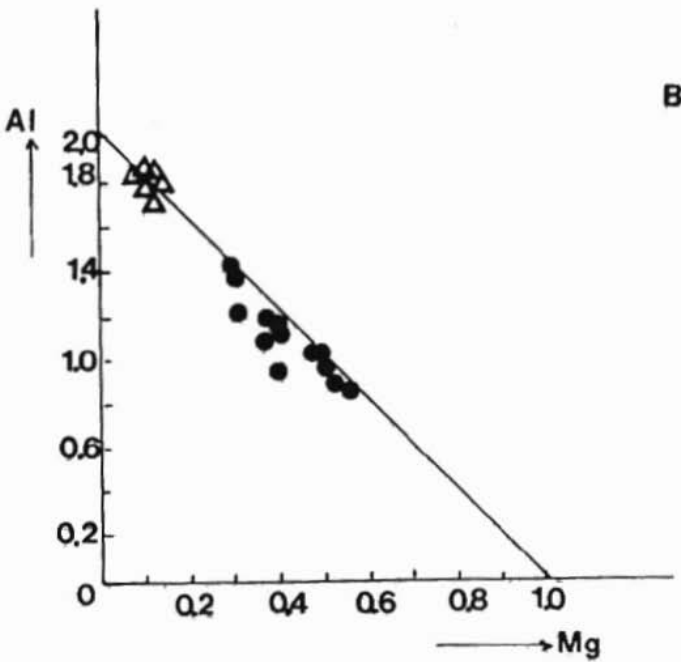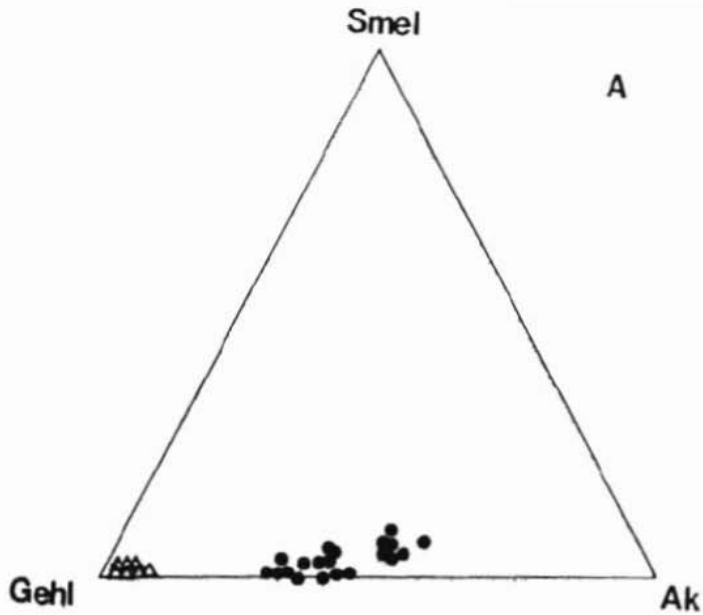
Fig.4: A: Chemical composition of melilite in relation to gehlenite (Gehl): akermamite (Ak): Na-melilite (Smel) components.
B: Al: Mg relationship in melilite (full circles) and gehlenite (trianges).

Vesuvianite

Representative compositions of the Maronia vesuvianite are listed in Table 2. The structural formula is calculated on the basis of 72 oxygen atoms. The FeO content in vesuvianite ranges between 1.8-4.2% and the MgO content between 2.8-3.4%.

Chlorite

Chlorite occurs in association with vesuvianite. Both minerals are formed as alteration products of melilite. Representative compositions of chlorite are given in Table 2. The structural formula is calculated on the basis of 28 oxygen atoms. Si ranges between 4.14-4.24, Al between 7.84-8.00, Mg between 7.25-7.69 and total iron as Fe^{2+} between 0.20-0.21 atoms p.f.u. According to Hey (1954) the chlorite is characterized as corundophyllite.

DISCUSSION

The Maronia monzogabbro represents a shallow intrusion which formed at the contact zones with the calcareous phyllites and the marbles high temperature calc-silicate hornfelses and skarns.

At the western contact zone, depending on the bulk rock composition of the parent rocks, the distance from the plutonic body, and the composition of the metasomatizing fluids the following rock types are distinguished:

a. Diopside-plagioclase-orthoclase hornfelses having the mineral assemblage:
   diopside-plagioclase-orthoclase-biotite-magnetite ± clinozoicite.
b. Clinopyroxene-wollastonite-grossular skarn with the mineral assemblage:
   grossular-wollastonite-diopsite-augite-calcite-orthoclase
c. Diopside-wollastonite-vesuvianite-grossular skarn with the mineral assemblage:
   grossular-wollastonite-diopside-calcite-vesuvianite.
   In this rock type diopside occurs in unoriented thin prismatic aggregates in association with calcite replasing pseudomorphically akermanite (?), while vesuvianite seems to be a hydration product of an earlier melilite.
d. Al-phlogopite-grossular skarn consisting predominantly of grossular and Al-phlogopite.
e. Augite-grossular skarn with the mineral assemblage:
   grossular-augite-calcite.
f. Melilitite skarn consisting predominantly of melilite. It is probably formed by the reaction of marble with the melt. Wollastonite, larnite and calcite occur as inclusions in melilite. Small vermicular grossular-andradite garnet occuring in the interstitial space of the melilite crystals, is possibly formed by reaction of the melilite rim with an oxydizing fluid.

The melilite skarns have been subjected to a retrograde metamorphism , recorded first by the decomposition of melilite into a fine grained aggregate consisting of gehlenite + monticellite + grossular. In a subsequent stage melilite is replaced by vesuvianite + corundophyllite.

The mineral parageneses observed in the skarn bodies can be studied in the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}CO_2\text{-}H_2O$ (ignoring the low iron content). In this system the P-T conditions of most reactions are strongly influenced by the composition of the fluid phase. Therefore a satisfactory approach to the temperature prevailing during the skarn formation requires a good knowledge of the composition of the fluid phase.

Fluid inclusions studied in garnet and vesuvianite (Doryphoros, 1990) indicate that both minerals were formed in a saline fluid medium with an equivalent salinity of 21-eq.wt% in NaCl. The homogenization temperatures corrected for a pressure of 1Kbar range between 535-633°C. The absence of visible fluid CO_2 ("double ring" Collins 1979, Roedder 1984) around the gas bubble indicates that the fluid was rich in H_2O with maximum $X_{CO_2} = 0.1$ (Kerrick 1977). A fluid inclusion study in melilite is not performed. Thus an estimation of the composition of the fluid phase during the melilite formation is still uncertain.

Figure 5 represents a $T\text{-}X_{CO_2}$ diagram at $P_f = 1Kbar$, of the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}CO_2\text{-}H_2O$
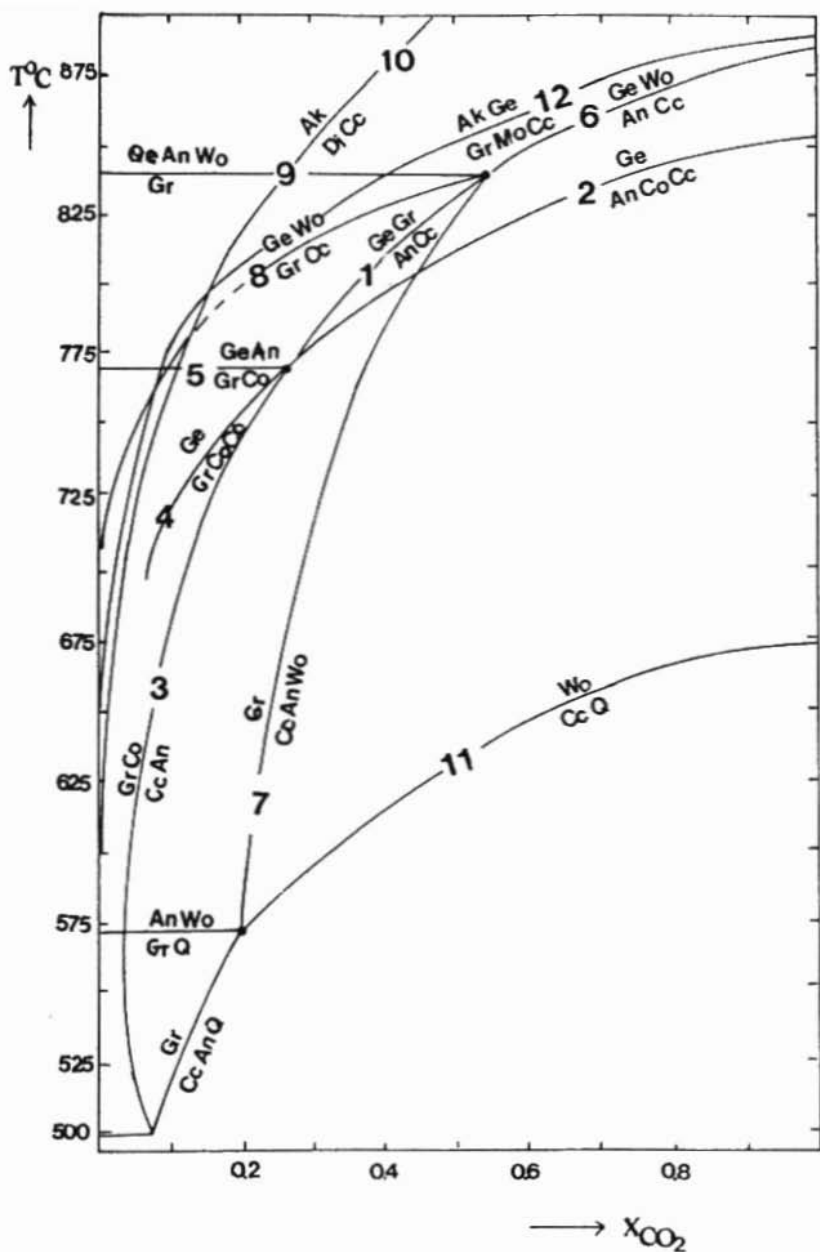
Fig.5: T-X$_{CO_2}$ diagram of the system CaO-Al$_2$O$_3$-SiO$_2$-CO$_2$-H$_2$O for Ps = 1kbar (after Hoscheck, 1974). Reaction curves 10,11 and 12 are calculated using the GEO-CALC software of Brown et al. (1988) and the thermodynamic database of Berman (1988). Cc=calcite, An = anorthite, Q = quartz, Wo = wollastonite, Gr = grossular, Co = corundum, Ge = gehlenite, Di = diopside, Ak = akermanite, Mo = monticellite.

with critical reactions determined experimentally by Hoschek (1974). In the same firure the reaction curves diopside + calcite = akermanite + CO_2 and grossular + monticellite + calcite = gehlenite + akermanite + CO_2, calculated using the GEO-CALC software of Brown et al. (1988) and the thermodynamic database of Berman (1988), are also shown.

The presence of larnite+calcite as inclusions in melilite indicates that the Maronia melilite skarn is formed at very high temperatures. According to experimental data given by Zharikow and Shmulovich (1969), (cited in Winkler, 1976), the formation of larnite at the expense of wollastonite+calcite requires a minimum temperature of $1000\text{-}1060^{\circ}C$, for a range of P_{CO2} 200-500 bars. This temperature falls to $900^{\circ}C$ if P_{CO2} is reduced to 50 bars. The above temperatures indicate that melilite is probably formed at temperatures higher than $900^{\circ}C$ supporting the textural evidence according to which the melilite skarn is formed by reaction of the marble with the melt.

In a retrograde stage of metamorphism, possibly with the influx of a water-rich fluid, melilite decomposes to gehlenite+monticellite+grossular. In this case the decomposition of melilite takes place according to the following reactions:

2akermanite + gehlenite + CO_2 = 2monticellite + grossular + calcite $\qquad$ (1) $\quad$ or

2akermanite + gehlenite + H_2O = 2monticellite + grossular + $Ca(OH)_2$ $\qquad$ (2)

Reaction (1) takes place for a pressure of 1 Kbar and X_{CO2} 0.2-0.4 at $800\text{-}840^{\circ}C$, (reaction 12, Fig.5), while raction (2) posibly at lower temperatures than reaction (1).

At still lower temperature melilite is decomposed by hydration to vesuvianite+corundophyllite. According to Ito and Arem (1970) the boundary separating the stability field of vesuvianite from melilite+H_2O lies between $600\text{-}700^{\circ}C$ for a pressure interval 0.5-2.5 Kbar. The Maronia vesuvianite seems to have formed within a temperature range $575\text{-}625^{\circ}C$. This temperature range is constrained by the boundary separating the stability field of vesuvianite from melilite+H_2O and the lowest values of the homogenization temperatures of fluid inclusions in vesuvianite. It must be noted that the highest homogenization temperatures are close to the value of $625^{\circ}C$.

In the diopside-wollastonite-vesuvianite-grossular skarn which is formed from a calcareous phyllite, temperatures of skarn fomation and composition of fluid phase can be estimated from mineral parageneses and textural relations using critital reactions shown in figure 5. The presence of wollastonite and calcite inclusions within garnet indicate temperatures in excess of $570^{\circ}C$ and X_{CO2} values above 0.2. (Fig.5, reaction 11) prevailing prior to the garnet formation. At this stage the rock probably was characterized by the paragenesis wollastonite+ calcite+diop-side+anorthite. With reduction of X_{CO2} in the fluid phase, probably resulting by influx of magmatic water, garnet and melilite are formed simultaneusly, the former according to reaction(7) and the latter by reaction (1) or (4) (Fig 5). In the case of reaction (4) corundum should have formed as an intermediate phase. Diopside reacted with calcite to form akermanite within the stability field of the paragenesis garnet+calcite. The formation of akermanite takes place below $775^{\circ}C$ at $X_{CO2} \approx 0.1$. The fluid inclusion study in garnet as well as in vesuvianite (Doryphoros, 1990) revealed X_{CO2} values in the fluid phase lower than 0.1. At lower temperatures the reaction diopside + calcite = akermanite + CO_2 proceeds from the right to the left forming diopside + calcite agregates pseudomorphically after akermanite. Vesuvianite is formed at still lower temperatures.

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